



(11)

EP 3 219 742 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:

20.09.2017 Bulletin 2017/38

(51) Int Cl.:

C08G 64/38 ^(2006.01) **C08G 64/18** ^(2006.01)
C08G 77/448 ^(2006.01) **C08L 69/00** ^(2006.01)

(21) Application number: **15840984.7**

(86) International application number:

PCT/KR2015/012291

(22) Date of filing: **16.11.2015**

(87) International publication number:

WO 2016/089024 (09.06.2016 Gazette 2016/23)

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

BA ME

Designated Validation States:

MA MD

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(30) Priority: **04.12.2014 KR 20140173005**

10.09.2015 KR 20150128296

13.11.2015 KR 20150159658

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(54) **COPOLYCARBONATE AND COMPOSITION CONTAINING SAME**

(57) The present invention relates to a copolycarbonate and a composition comprising the same. The copolycarbonates according to the present invention has a structure in which a specific siloxane compound is introduced in a main chain of the polycarbonate, and thus exhibits improved chemical resistance and impact strength simultaneously.

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Description**[CROSS-REFERENCE TO RELATED APPLICATION(S)]**

[0001] This application claims the benefit of Korean Patent Application No. 10-2014-0173005 filed on December 4, 2014, Korean Patent Application No. 10-2015-0128296 filed on September 10, 2015 and Korean Patent Application No. 10-2015-0159658 filed on November 13, 2015 with the Korean Intellectual Property Office, the disclosures of which are incorporated herein by reference in their entirety.

[TECHNICAL FIELD]

[0002] The present invention relates to a copolycarbonate and a composition comprising the same, and more specifically to a copolycarbonate being economically produced, and having improved chemical resistance and impact strength simultaneously, and to a composition comprising the same.

[BACKGROUND OF ART]

[0003] Polycarbonate resins are prepared by condensation-polymerization of an aromatic diol such as bisphenol A with a carbonate precursor such as a phosgene and have excellent impact strength, dimensional stability, heat resistance and transparency. Thus, the polycarbonate resins have application in a wide range of uses, such as exterior materials of electrical and electronic products, automobile parts, building materials, and optical components.

[0004] Recently, in order to apply these polycarbonate resins to more various fields, many studies have been made to obtain desired physical properties by copolymerizing two or more aromatic diol compounds having different structures from each other and introducing units having different structures in a main chain of the polycarbonate.

[0005] Especially, studies for introducing a polysiloxane structure in a main chain of the polycarbonate have been undergone, but most of these technologies have disadvantages in that production costs are high, and the chemical resistance and the impact strength are not improved simultaneously.

[0006] Given the above circumstances, the present inventors have conducted intensive studies to overcome the above-mentioned disadvantages encountered with the prior arts and develop a copolycarbonate having improved chemical resistance and impact strength simultaneously, and found that a copolycarbonate in which a specific siloxane compound is introduced in a main chain of the polycarbonate as described below satisfies the above-described properties. The present invention has been completed on the basis of such a finding.

[DETAILED DESCRIPTION OF THE INVENTION]**[Technical Problem]**

[0007] It is an object of the present invention to provide a copolycarbonate having improved chemical resistance and impact strength simultaneously.

[0008] It is another object of the present invention to provide a polycarbonate composition comprising the above-mentioned copolycarbonate and a polycarbonate.

[0009] It is a further object of the present invention to provide an article comprising the above-mentioned copolycarbonate or the polycarbonate composition.

[Technical Solution]

[0010] In order to achieve these objects, the present invention provides a copolycarbonate which comprises an aromatic polycarbonate-based first repeating unit; and one or more aromatic polycarbonate-based second repeating units having siloxane bonds, and satisfies the following Equation 1:

[Equation 1]

$$TS/TS_0 \geq 0.80$$

in the Equation 1,

TS_0 is tensile stress measured in accordance with ASTM D638, and

TS represents tensile stress measured in accordance with ASTM D638, after contacted with ethyl acetate for 168 hours in accordance with ASTM D543 (PRACTICE B).

[0011] As used herein, Equation 1 refers to chemical resistance of the copolycarbonate according to the present invention, which means a change in the tensile stress caused by contacting of the copolycarbonate with a specific solvent for a specific period of time. If TS/TS_0 in the Equation 1 is 1, it means that there is no change in the tensile stress of the copolycarbonate regardless of a specific solvent contacted with. Therefore, this means that as the value of TS/TS_0 increases, the chemical resistance is excellent.

[0012] In particular, the copolycarbonate according to the present invention has a low change in the tensile stress, particularly when contacted with ethyl acetate. Preferably, in the Equation 1, TS/TS_0 is not less than 0.81, not less than 0.82, not less than 0.83, not less than 0.84, not less than 0.85, not less than 0.86, not less than 0.87, not less than 0.88, not less than 0.89, or not less than 0.90. Further, in the Equation 1, TS/TS_0 may be, for example, not more than 1, or not more than 0.99.

[0013] In addition, the copolycarbonate according to the present invention has a low change in the tensile stress even when contacted with toluene in addition to ethyl acetate. Specifically, the copolycarbonate according to the present invention satisfies the Equation 2 below:

[Equation 2]

$$TS/TS_0 \geq 0.50$$

in the above Equation 2,

TS_0 is tensile stress measured in accordance with ASTM D638, and TS represents tensile stress measured in accordance with ASTM D638, after contacted with toluene for 168 hours in accordance with ASTM D543 (PRACTICE B).

[0014] Preferably, in the Equation 2, TS/TS_0 is not less than 0.51, not less than 0.52, not less than 0.53, not less than 0.54, or not less than 0.55. In addition, in the Equation 2, TS/TS_0 may be, for example, not more than 1, not more than 0.99, not more than 0.98, not more than 0.97, not more than 0.96, or not more than 0.95.

[0015] The copolycarbonate according to the present invention has a low change in the tensile strength even when contacted with hydrochloric acid, sodium hydroxide, or methanol in addition to ethyl acetate and toluene. When TS/TS_0 is applied to hydrochloric acid, sodium hydroxide or methanol as shown in Equation 1 or 2, the value is not less than 0.95 and not more than 1.

[0016] Further, the copolycarbonate according to the present invention has excellent impact strength, for example, impact strength at low temperature and impact strength at room temperature in addition to the above-described excellent chemical resistance.

[0017] The impact strength at low temperature is measured at -30°C in accordance with ASTM D256 (1/8 inch, Notched Izod). Preferably, the impact strength at low temperature is not less than 600 J/m, not less than 650 J/m, not less than 700 J/m, not less than 710 J/m, not less than 720 J/m, not less than 730 J/m, not less than 740 J/m, or not less than 750 J/m. In addition, the impact strength at low temperature is excellent when the value is higher, and thus it is not limited to any upper limit value. As one example, however, it may be not more than 990 J/m, not more than 980 J/m, not more than 970 J/m, not more than 960 J/m, not more than 950 J/m, not more than 940 J/m, not more than 930 J/m, not more than 920 J/m or not more than 910 J/m.

[0018] The impact strength at room temperature is measured in accordance with ASTM D256 (1/8 inch, Notched Izod). Preferably, the impact strength at room temperature is not less than 850 J/m, not less than 860 J/m, not less than 870 J/m, not less than 880 J/m, not less than 890 J/m, not less than 900 J/m, not less than 910 J/m, not less than 920 J/m, not less than 930 J/m, not less than 940 J/m, not less than 950 J/m, or not less than 960 J/m. Further, the impact strength at room temperature is excellent when the value is higher, and thus it is not limited to any upper limit value. As one example, however, it may be not more than 990 J/m, not more than 980 J/m, or not more than 970 J/m.

[0019] Further, the copolycarbonate according to the present invention has a weight average molecular weight of 1,000 to 100,000 g/mol, and preferably 15,000 to 35,000 g/mol.

[0020] More preferably, the above weight average molecular weight is not less than 20,000 g/mol, not less than 21,000 g/mol, not less than 22,000 g/mol, not less than 23,000 g/mol, not less than 24,000 g/mol, not less than 25,000 g/mol, not less than 26,000 g/mol, not less than 27,000 g/mol, or not less than 28,000 g/mol. Further, the above weight average molecular weight is not more than 34,000 g/mol, not more than 33,000 g/mol, not more than 32,000 g/mol, or not more than 31,000 g/mol.

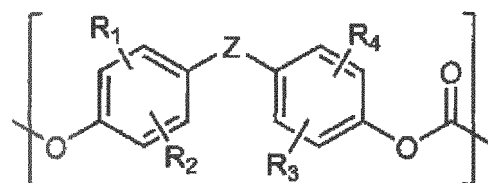
[0021] Further, preferably, the copolycarbonate according to the present invention has a melt index of 3 to 10 as measured in accordance with ASTM D1238 (conditions of 300 °C and 1.2 kg). Preferably, the melt index is not less than 4, not less than 5, or not less than 6; and not more than 9, or not more than 8.

[0022] Further, preferably, the copolycarbonate according to the present invention may comprise two kinds of aromatic polycarbonate-based second repeating units having siloxane bonds.

[0023] Further, in the copolycarbonate according to the present invention, the mole ratio of the aromatic polycarbonate-based first repeating unit and the one or more aromatic polycarbonate-based second repeating units having siloxane bonds may be preferably 1:0.001-0.006, and/or the weight ratio thereof may be 1:0.01-0.03.

[0024] Further, in the copolycarbonate according to the present invention, specifically, the aromatic polycarbonate-based first repeating unit is formed by reacting an aromatic diol compound and a carbonate precursor, and it may be preferably represented by the following Chemical Formula 1:

[Chemical Formula 1]



in the Chemical Formula 1,

R_1 , R_2 , R_3 , and R_4 are each independently hydrogen, C_{1-10} alkyl, C_{1-10} alkoxy, or halogen, and

Z is C_{1-10} alkylene unsubstituted or substituted with phenyl, C_{3-15} cycloalkylene unsubstituted or substituted with C_{1-10} alkyl, O, S, SO, SO_2 , or CO.

[0025] Preferably, in the Chemical Formula 1, R_1 , R_2 , R_3 , and R_4 are each independently hydrogen, methyl, chloro, or bromo.

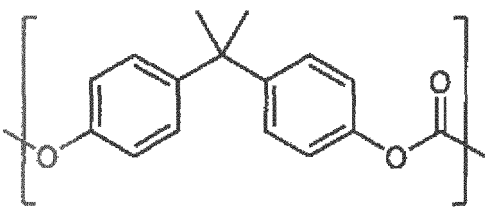
[0026] Further, Z is preferably a linear or branched C_{1-10} alkylene unsubstituted or substituted with phenyl, and more preferably methylene, ethane-1,1-diyl, propane-2,2-diyl, butane-2,2-diyl, 1-phenylethane-1,1-diyl, or diphenylmethylene. Further, preferably, Z is cyclohexane-1,1-diyl, O, S, SO, SO_2 , or CO.

[0027] Preferably, the repeating unit represented by Chemical Formula 1 may be derived from one or more aromatic diol compounds selected from the group consisting of bis(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl)ether, bis(4-hydroxyphenyl)sulfone, bis(4-hydroxyphenyl)sulfoxide, bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)ketone, 1,1-bis(4-hydroxyphenyl)ethane, bisphenol A, 2,2-bis(4-hydroxyphenyl)butane, 1,1-bis(4-hydroxyphenyl)cyclohexane, 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane, 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane, 2,2-bis(4-hydroxy-3-bromophenyl)propane, 2,2-bis(4-hydroxy-3-chlorophenyl)propane, 2,2-bis(4-hydroxy-3-methylphenyl)propane, 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, bis(4-hydroxyphenyl)diphenylmethane, and α,ω -bis[3-(o-hydroxyphenyl)propyl]polydimethylsiloxane.

[0028] As used herein, "derived from aromatic diol compounds" means that a hydroxy group of the aromatic diol compound and a carbonate precursor are reacted to form the repeating unit represented by Chemical Formula 1.

[0029] For example, when bisphenol A, which is an aromatic diol compound, and triphosgene, which is a carbonate precursor, are polymerized, the repeating unit represented by Chemical Formula 1 is represented by the following Chemical Formula 1-1:

[Chemical Formula 1-1]

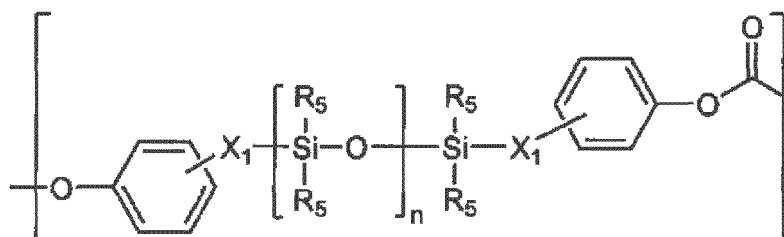


[0030] The carbonate precursor used herein may include one or more selected from the group consisting of dimethyl carbonate, diethyl carbonate, dibutyl carbonate, dicyclohexyl carbonate, diphenyl carbonate, ditolyl carbonate, bis(chlo-

rophenyl) carbonate, di-m-cresyl carbonate, dinaphthyl carbonate, bis(diphenyl) carbonate, phosgene, triphosgene, diphosgene, bromo phosgene and bishaloformate. Preferably, triphosgene or phosgene may be used.

[0031] Further, in the copolycarbonate according to the present invention, the one or more aromatic polycarbonate-based second repeating units having siloxane bonds are formed by reacting one or more siloxane compounds and a carbonate precursor, and they may comprise preferably a repeating unit represented by the following Chemical Formula 2 and a repeating unit represented by the following Chemical Formula 3:

[Chemical Formula 2]

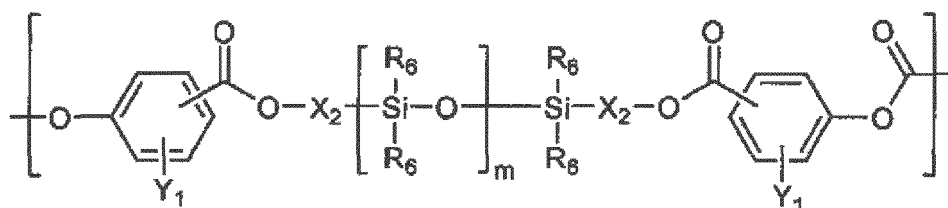


in the Chemical Formula 2,

each of X_1 is independently C_{1-10} alkylene,

each of R_5 is independently hydrogen; C_{1-15} alkyl unsubstituted or substituted with oxiranyl, oxiranyl-substituted C_{1-10} alkoxy, or C_{6-20} aryl; halogen; C_{1-10} alkoxy; allyl; C_{1-10} haloalkyl; or C_{6-20} aryl, and n is an integer of 10 to 200,

[Chemical Formula 3]



in the Chemical Formula 3,

each of X_2 is independently C_{1-10} alkylene,

each of Y_1 is independently hydrogen, C_{1-6} alkyl, halogen, hydroxy, C_{1-6} alkoxy, or C_{6-20} aryl,

each of R_6 is independently hydrogen; or C_{1-15} alkyl unsubstituted or substituted with oxiranyl, oxiranyl-substituted C_{1-10} alkoxy, or C_{6-20} aryl; halogen; C_{1-10} alkoxy; allyl; C_{1-10} haloalkyl; or C_{6-20} aryl, and m is an integer of 10 to 200.

[0032] In the Chemical Formula 2, each of X_1 is independently preferably C_{2-10} alkylene, more preferably C_{2-4} alkylene, and most preferably propane-1,3-diyl.

[0033] Also, preferably, each of R_5 is independently hydrogen, methyl, ethyl, propyl, 3-phenylpropyl, 2-phenylpropyl, 3-(oxiranylmethoxy)propyl, fluoro, chloro, bromo, iodo, methoxy, ethoxy, propoxy, allyl, 2,2,2-trifluoroethyl, 3,3,3-trifluoropropyl, phenyl, or naphthyl. In addition, each of R_5 is independently preferably C_{1-10} alkyl, more preferably C_{1-6} alkyl, more preferably C_{1-3} alkyl and most preferably methyl.

[0034] Further, preferably, n is an integer of not less than 10, not less than 15, not less than 20, not less than 25, not less than 30, not less than 31, or not less than 32; and not more than 50, not more than 45, not more than 40, not more than 39, not more than 38, or not more than 37.

[0035] In the Chemical Formula 3, each of X_2 is independently preferably C_{2-10} alkylene, more preferably C_{2-6} alkylene, and most preferably isobutylene.

[0036] Further, preferably, Y_1 is hydrogen.

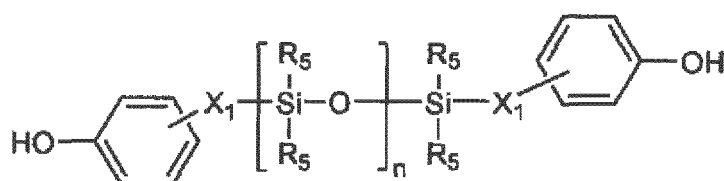
[0037] Further, preferably, each of R_6 is independently hydrogen, methyl, ethyl, propyl, 3-phenylpropyl, 2-phenylpropyl, 3-(oxiranylmethoxy)propyl, fluoro, chloro, bromo, iodo, methoxy, ethoxy, propoxy, allyl, 2,2,2-trifluoroethyl, 3,3,3-trifluoropropyl, phenyl, or naphthyl. Further, preferably, each of R_6 is independently C_{1-10} alkyl, more preferably C_{1-6} alkyl,

more preferably C₁₋₃ alkyl, and most preferably methyl.

[0038] Preferably, m is an integer of not less than 40, not less than 45, not less than 50, not less than 55, not less than 56, not less than 57, or not less than 58; and not more than 80, not more than 75, not more than 70, not more than 65, not more than 64, not more than 63, or not more than 62.

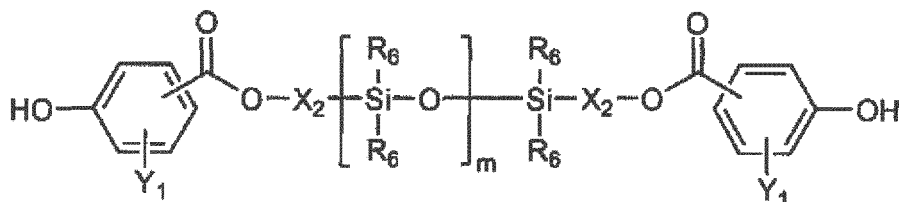
[0039] The repeating unit represented by Chemical Formula 2 and the repeating unit represented by Chemical Formula 3 are, derived from a siloxane compound represented by the following Chemical Formula 2-1 and a siloxane compound represented by the following Chemical Formula 3-1, respectively:

[Chemical Formula 2-1]



in the Chemical Formula 2-1, X₁, R₅ and n are the same as previously defined.

[Chemical Formula 3-1]

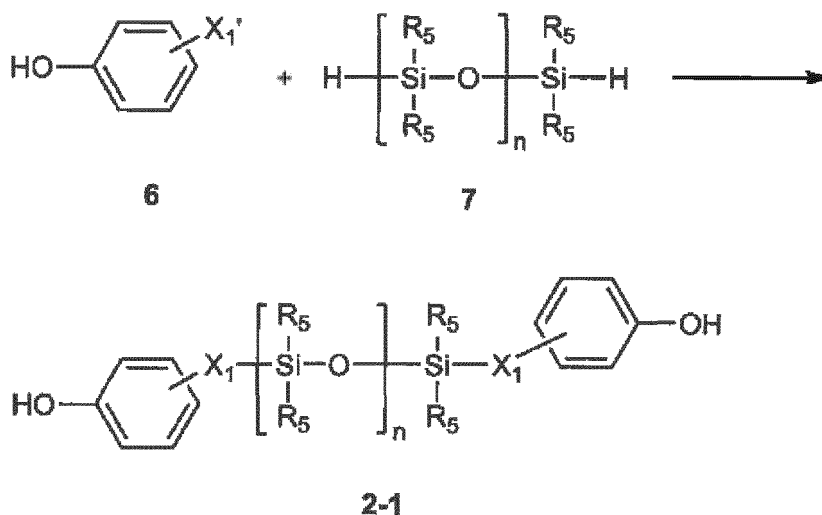


in the Chemical Formula 3-1, X₂, Y₁, R₆ and m are the same as previously defined.

[0040] As used herein, "derived from a siloxane compound" means that a hydroxy group of the respective siloxane compound and a carbonate precursor are reacted to form the repeating unit represented by Chemical Formula 2 and the repeating unit represented by Chemical Formula 3. Further, the carbonate precursors that can be used for the formation of the repeating units represented by Chemical Formulae 2 and 3 are the same as those described for the carbonate precursor that can be used for the formation of the repeating unit represented by Chemical Formula 1 described above.

[0041] The methods for preparing the siloxane compound represented by Chemical Formula 2-1 and the siloxane compound represented by Chemical Formula 3-1 are represented by the following Reaction Schemes 1 and 2:

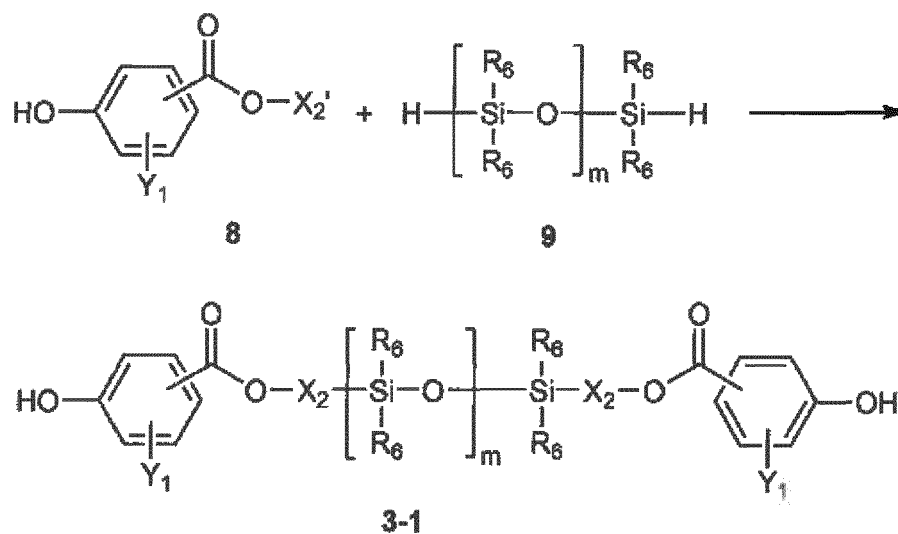
[Reaction Scheme 1]



in the Reaction Scheme 1,

X_1' is C_{2-10} alkenyl, and
 X_1 , R_5 and n are as previously defined,

[Reaction Scheme 2]



in the Reaction Scheme 2,

X_2' is C_{2-10} alkenyl, and
 X_2 , Y_1 , R_6 and m are as previously defined.

[0042] In the Reaction Scheme 1 and Reaction Scheme 2, the reaction is preferably conducted in the presence of a metal catalyst. As the metal catalyst, a Pt catalyst is preferably used. The Pt catalyst used herein may include one or more selected from the group consisting of Ashby catalyst, Karstedt catalyst, Lamoreaux catalyst, Speier catalyst, $\text{PtCl}_2(\text{COD})$, $\text{PtCl}_2(\text{benzonitrile})_2$ and H_2PtBr_6 . The metal catalyst may be used in an amount of not less than 0.001 parts by weight, not less than 0.005 parts by weight, or not less than 0.01 parts by weight; and not more than 1 part by weight, not more than 0.1 part by weight, or not more than 0.05 part by weight, based on 100 parts by weight of the compounds represented by the Chemical Formulae 7 or 9.

[0043] Further, the above reaction temperature is preferably 80 to 100°C. Further, the above reaction time is preferably 1 to 5 hours.

[0044] In addition, the compounds represented by Chemical Formulae 7 or 9 can be prepared by reacting an organ-

odisiloxane and an organocyclosiloxane in the presence of an acid catalyst, and n and m may be adjusted by adjusting the amount of the reactants used. The reaction temperature is preferably 50 to 70°C. Also, the reaction time is preferably 1 to 6 hours.

[0045] The above organodisiloxane may include one or more selected from the group consisting of tetramethyldisiloxane, tetraphenyldisiloxane, hexamethyldisiloxane and hexaphenyldisiloxane. In addition, the above organocyclosiloxane may include, for example, organocyclotetrasiloxane. As one example thereof, octamethylcyclotetrasiloxane, octaphenylcyclotetrasiloxane or the like may be included.

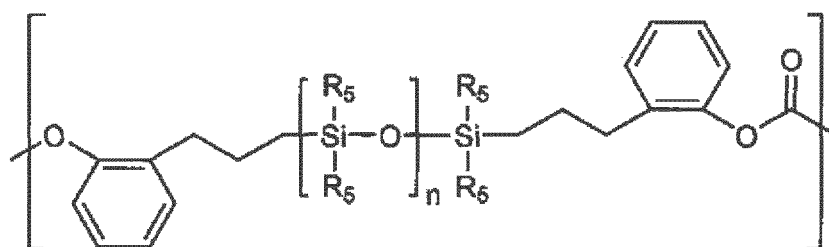
[0046] The above organodisiloxane may be used in an amount of not less than 0.1 parts by weight, or not less than 2 parts by weight; and not more than 10 parts by weight or not more than 8 parts by weight, based on 100 parts by weight of the organocyclosiloxane.

[0047] The above acid catalyst that may be used herein includes one or more selected from the group consisting of H_2SO_4 , HClO_4 , AlCl_3 , SbCl_5 , SnCl_4 and acid clay (fuller's earth). Further, the acid catalyst may be used in an amount of not less than 0.1 parts by weight, not less than 0.5 parts by weight, or not less than 1 part by weight; and not more than 10 parts by weight, not more than 5 parts by weight or not more than 3 parts by weight, based on 100 parts by weight of the organocyclosiloxane.

[0048] In particular, by adjusting the content of the repeating unit represented by Chemical Formula 2 and the repeating unit represented by Chemical Formula 3, the chemical resistance and the impact strength of the copolycarbonate can be improved simultaneously. Preferably, the weight ratio between the above repeating units may be from 1:99 to 99:1. Preferably, the weight ratio is from 3:97 to 97:3, from 5:95 to 95:5, from 10:90 to 90:10, or from 15:85 to 85:15, and more preferably from 20:80 to 80:20. The weight ratios of the above repeating units correspond to the weight ratios of siloxane compounds, for example, the siloxane compound represented by Chemical Formula 2-1 and the siloxane compound represented by Chemical Formula 3-1,

[0049] Preferably, the repeating unit represented by Chemical Formula 2 is represented by the following Chemical Formula 2-2:

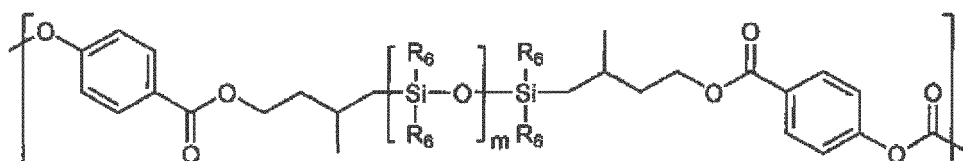
[Chemical Formula 2-2]



in the Chemical Formula 2-2, R_5 and n are the same as previously defined. Preferably, R_5 is methyl.

[0050] Also, preferably, the repeating unit represented by Chemical Formula 3 is represented by the following Chemical Formula 3-2:

[Chemical Formula 3-2]



in the Chemical Formula 3-2, R_6 and m are the same as previously defined. Preferably, R_6 is methyl.

[0051] Further, preferably, the copolycarbonate according to the present invention comprises all of the repeating unit represented by Chemical Formula 1-1, the repeating unit represented by Chemical Formula 2-2, and the repeating unit represented by Chemical Formula 3-2.

[0052] Further, the present invention provides a method for preparing a copolycarbonate comprising a step of polymerizing the aromatic diol compound, the carbonate precursor and one or more siloxane compounds.

[0053] The aromatic diol compound, the carbonate precursor and one or more siloxane compounds are the same as previously described.

[0054] During the polymerization, one or more siloxane compounds may be used in an amount of not less than 0.1% by weight, not less than 0.5% by weight, not less than 1% by weight, or not less than 1.5% by weight; and not more than

20% by weight, not more than 10% by weight, not more than 7% by weight, not more than 5% by weight, not more than 4% by weight, not more than 3% by weight, or not more than 2% by weight, based on 100% by weight in total of the aromatic diol compound, the carbonate precursor and one or more siloxane compounds. Also, the above aromatic diol compound may be used in an amount of not less than 40% by weight, not less than 50% by weight, or not less than 55% by weight; and not more than 80% by weight, not more than 70% by weight, or not more than 65% by weight, based on 100% by weight in total of the aromatic diol compound, the carbonate precursor and one or more siloxane compounds. The above carbonate precursor may be used in an amount of not less than 10% by weight, not less than 20% by weight, or not less than 30% by weight; and not more than 60% by weight, not more than 50% by weight, or not more than 40% by weight, based on 100% by weight in total of the aromatic diol compound, the carbonate precursor and the one or more siloxane compounds.

[0055] Further, as the polymerization method, an interfacial polymerization method may be used as one example. In this case, there is an effect in that the polymerization reaction is possible at a low temperature and an atmospheric pressure, and thus control of molecular weight is easy. The above interfacial polymerization is preferably conducted in the presence of an acid binder and an organic solvent. Furthermore, the above interfacial polymerization may comprise, for example, the steps of conducting pre-polymerization, then adding a coupling agent and conducting polymerization again. In this case, the copolycarbonate having a high molecular weight may be obtained.

[0056] The materials used in the interfacial polymerization are not particularly limited as long as they may be used in the polymerization of polycarbonates. The used amount thereof may be controlled as required.

[0057] The acid binding agent may include, for example, alkali metal hydroxides such as sodium hydroxide or potassium hydroxide, or amine compounds such as pyridine.

[0058] The organic solvent is not particularly limited as long as it is a solvent that may be usually used in the polymerization of polycarbonate. As one example, halogenated hydrocarbon such as methylene chloride or chlorobenzene may be used.

[0059] Further, during the interfacial polymerization, a reaction accelerator, for example, a tertiary amine compound such as triethylamine, tetra-n-butyl ammonium bromide and tetra-n-butylphosphonium bromide, a quaternary ammonium compound or a quaternary phosphonium compound may be further used for accelerating the reaction.

[0060] In the interfacial polymerization, the reaction temperature is preferably from 0 to 40°C and the reaction time is preferably from 10 minutes to 5 hours. Further, during the interfacial polymerization reaction, pH is preferably maintained at 9 or more, or 11 or more.

[0061] In addition, the interfacial polymerization may be conducted by further including a molecular weight modifier. The molecular weight modifier may be added before the initiation of polymerization, during the initiation of polymerization, or after the initiation of polymerization.

[0062] As the above molecular weight modifier, mono-alkylphenol may be used. As one example, the mono-alkylphenol is one or more selected from the group consisting of p-tert-butylphenol, p-cumyl phenol, decyl phenol, dodecyl phenol, tetradecyl phenol, hexadecyl phenol, octadecyl phenol, eicosyl phenol, docosyl phenol and triacontyl phenol, and preferably p-tert-butylphenol. In this case, the effect of adjusting the molecular weight control is great.

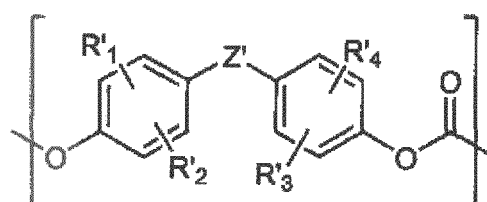
[0063] The above molecular weight modifier is contained, for example, in an amount of not less than 0.01 parts by weight, not less than 0.1 parts by weight, or not less than 1 part by weight; and not more than 10 parts by weight, not more than 6 parts by weight, or not more than 5 parts by weight, based on 100 parts by weight of the aromatic diol compound. Within this range, the required molecular weight may be obtained.

[0064] In addition, the present invention provides a polycarbonate composition comprising the above-mentioned copolycarbonate and polycarbonate. The copolycarbonate may be used alone, but it may be used together with the polycarbonate as needed to control the physical property of the copolycarbonate.

[0065] The above polycarbonate is distinguished from the copolycarbonate according to the present invention in that a polysiloxane structure is not introduced in a main chain of the polycarbonate.

[0066] Preferably, the above polycarbonate comprises a repeating unit represented by the following Chemical Formula 4:

[Chemical Formula 4]



In the Chemical Formula 4,

R'_1 , R'_2 , R'_3 and R'_4 are each independently hydrogen, C_{1-10} alkyl, C_{1-10} alkoxy or halogen, and Z' is C_{1-10} alkylene unsubstituted or substituted with phenyl, C_{3-15} cycloalkylene unsubstituted or substituted with C_{1-10} alkyl, O, S, SO, SO_2 or CO.

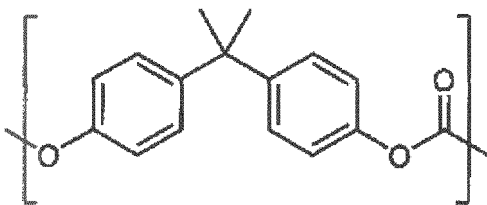
[0067] Further, preferably, the above polycarbonate has a weight average molecular weight of 15,000 to 35,000 g/mol. More preferably, the above weight average molecular weight is not less than 20,000 g/mol, not less than 21,000 g/mol, not less than 22,000 g/mol, not less than 23,000 g/mol, not less than 24,000 g/mol, not less than 25,000 g/mol, not less than 26,000 g/mol, not less than 27,000 g/mol, or not less than 28,000 g/mol. Further, the above weight average molecular weight is not more than 34,000 g/mol, not more than 33,000 g/mol, or not more than 32,000 g/mol.

[0068] The repeating unit represented by Chemical Formula 4 is formed by reacting the aromatic diol compound and the carbonate precursor. The aromatic diol compound and the carbonate precursor that may be used herein are the same as previously described for the repeating unit represented by Chemical Formula 1.

[0069] Preferably, R'_1 , R'_2 , R'_3 , R'_4 and Z' in Chemical Formula 4 are the same as previously described for R_1 , R_2 , R_3 , R_4 and Z in Chemical Formula 1, respectively.

[0070] Further, preferably, the repeating unit represented by Chemical Formula 4 is represented by the following Chemical Formula 4-1:

[Chemical Formula 4-1]



[0071] In addition, the present invention provides an article comprising the above-mentioned copolycarbonate or the polycarbonate composition.

[0072] Preferably, the above article is an injection molded article. In addition, the article may further comprise, for example, one or more selected from the group consisting of antioxidants, heat stabilizers, light stabilizers, plasticizers, antistatic agents, nucleating agents, flame retardants, lubricants, impact reinforcing agents, fluorescent brightening agents, ultraviolet absorbers, pigments and dyes.

[0073] The method for preparing the article may comprise the steps of mixing the copolycarbonate according to the present invention and additives such as antioxidants with a mixer, extrusion-molding the mixture with an extruder to produce a pellet, drying the pellet and then injecting the dried pellet with an injection molding machine.

[ADVANTAGEOUS EFFECTS]

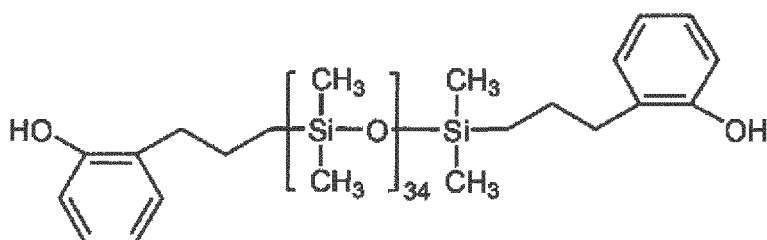
[0074] As set forth above, according to the present invention, the copolycarbonate in which a specific siloxane compound is introduced in a main chain of the polycarbonate has an effect of improving chemical resistance and impact strength simultaneously.

[DETAILED DESCRIPTION OF THE EMBODIMENTS]

[0075] Below, preferred embodiments will be provided in order to assist in the understanding of the present disclosure. However, these examples are provided only for illustration of the present invention, and should not be construed as limiting the present invention to these examples.

Preparation Example 1: AP-PDMS(n=34)

[0076]

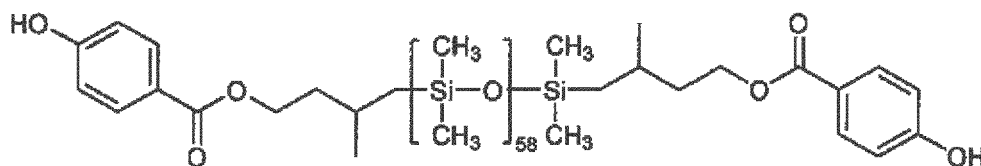


[0077] 47.60 g (160 mmol) of octamethylcyclotetrasiloxane and 2.40 g (17.8 mmol) of tetramethyldisiloxane were mixed. The mixture was then placed in 3L flask together with 1 part by weight of acid clay (DC-A3) compared to 100 parts by weight of octamethylcyclotetrasiloxane, and reacted at 60°C for 4 hours. After completion of the reaction, the reaction product was diluted with ethyl acetate and quickly filtered using a celite. The repeating unit (n) of the terminal-unmodified polyorganosiloxane thus prepared was 34 when confirmed through ¹H NMR.

[0078] To the resulting terminal-unmodified polyorganosiloxane, 4.81 g (35.9 mmol) of 2-allylphenol and 0.01 g (50 ppm) of Karstedt's platinum catalyst were added and reacted at 90°C for 3 hours. After completion of the reaction, the unreacted siloxane was removed by conducting evaporation under the conditions of 120°C and 1 torr. The terminal-modified polyorganosiloxane thus prepared was designated as AP-PDMS (n = 34). AP-PDMS was a pale yellow oil and the repeating unit (n) was 34 when confirmed through ¹H NMR using a Varian 500MHz, and further purification was not required.

Preparation Example 2: MBHB-PDMS(m=58)

[0079]

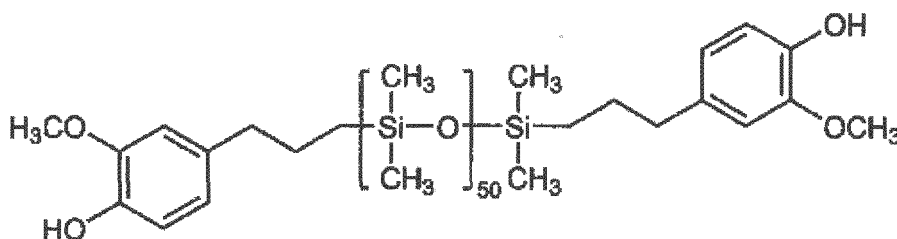


[0080] 47.60 g (160 mmol) of octamethylcyclotetrasiloxane and 1.5 g (11 mmol) of tetramethyldisiloxane were mixed. The mixture was then introduced in 3L flask together with 1 part by weight of acid clay (DC-A3) compared to 100 parts by weight of octamethylcyclotetrasiloxane, and reacted at 60°C for 4 hours. After completion of the reaction, the reaction product was diluted with ethyl acetate and quickly filtered using a celite. The repeating unit (m) of the terminal-unmodified polyorganosiloxane thus prepared was 58 when confirmed through ¹H NMR.

[0081] To the resulting terminal-unmodified polyorganosiloxane, 6.13 g (29.7 mmol) of 3-methylbut-3-enyl 4-hydroxybenzoate and 0.01 g (50 ppm) of Karstedt's platinum catalyst were added and reacted at 90°C for 3 hours. After completion of the reaction, the unreacted siloxane was removed by conducting evaporation under the conditions of 120°C and 1 torr. The terminal-modified polyorganosiloxane thus prepared was designated as MBHB-PDMS(m=58). MBHB-PDMS was pale yellow oil and the repeating unit (m) was 58 when confirmed through ¹H NMR using a Varian 500MHz, and further purification was not required.

Preparation Example 3: Eugenol-PDMS

[0082]



[0083] 47.60 g (160 mmol) of octamethylcyclotetrasiloxane and 1.7 g (13 mmol) of tetramethyldisiloxane were mixed.

The mixture was then placed in 3L flask together with 1 part by weight of acid clay (DC-A3) compared to 100 parts by weight of octamethylcyclotetrasiloxane, and reacted at 60°C for 4 hours. After completion of the reaction, the reaction product was diluted with ethyl acetate and quickly filtered using a celite. The repeating unit (n) of the terminal-unmodified polyorganosiloxane thus prepared was 50 when confirmed through ¹H NMR.

[0084] To the resulting terminal-unmodified polyorganosiloxane, 6.13 g (29.7 mmol) of Eugenol and 0.01 g (50 ppm) of Karstedt's platinum catalyst were added and reacted at 90°C for 3 hours. After completion of the reaction, the unreacted siloxane was removed by conducting evaporation under the conditions of 120°C and 1 torr. The terminal-modified polyorganosiloxane thus prepared was designated as Eugenol-PDMS. Eugenol-PDMS was pale yellow oil and the repeating unit (n) was 50 when confirmed through ¹H NMR using a Varian 500MHz, and further purification was not required.

Example 1

[0085] 1784 g of water, 385 g of NaOH and 232 g of BPA (bisphenol A) were introduced in a polymerization reactor, and dissolved with mixing under a N₂ atmosphere. 4.3 g of PTBP (para-tert butylphenol) and the mixed solution (weight ratio of 90:10) of 5.91 g of AP-PDMS (n=34) prepared in Preparation Example 1 and 0.66 g of MBHB-PDMS (m=58) prepared in Preparation Example 2 were dissolved in MC (methylene chloride) and added thereto. Subsequently, 128 g of TPG (triphosgene) was dissolved in MC and a dissolved TPG solution was added thereto and reacted for 1 hour while maintaining pH of the TPG solution at 11 or more. After 10 minutes, 46 g of TEA (triethylamine) was added thereto to conduct a coupling reaction. After a total reaction time of 1 hour and 20 minutes, pH was lowered to 4 to remove TEA, and pH of a produced polymer was adjusted to neutral pH of 6 to 7 by washing three times with distilled water. The polymer obtained was re-precipitated in a mixed solution of methanol and hexane, and then dried at 120°C to give a final copolycarbonate.

Example 2

[0086] The copolycarbonate was prepared in the same method as in Example 1, except that the mixed solution (weight ratio of 95:5) of 6.24 g of AP-PDMS (n=34) prepared in Preparation Example 1 and 0.33 g of MBHB-PDMS (m=58) prepared in Preparation Example 2 was used.

Comparative Example 1

[0087] 1784 g of water, 385 g of NaOH and 232 g of BPA (bisphenol A) were added to a polymerization reactor, and dissolved with mixing under a N₂ atmosphere. 4.3 g of PTBP (para-tert butylphenol) and 6.57 g of AP-PDMS prepared in Preparative Example 1 were dissolved in MC (methylene chloride) and added thereto. Subsequently, 128 g of TPG (triphosgene) was dissolved in MC and a dissolved TPG solution added thereto and reacted for 1 hour while maintaining pH of the TPG solution at 11 or more. After 10 minutes, 46 g of TEA (triethylamine) was added thereto to conduct a coupling reaction. After a total reaction time of 1 hour and 20 minutes, pH was lowered to 4 to remove TEA, and pH of a produced polymer was adjusted to neutral pH of 6 to 7 by washing three times with distilled water. The polymer obtained was re-precipitated in a mixed solution of methanol and hexane, and then dried at 120°C to give a final copolycarbonate.

Comparative Example 2

[0088] The copolycarbonate was prepared by the same method as in Comparative Example 1, except that Eugenol-PDMS prepared in Preparation Example 3 instead of AP-PDMS (n=34) prepared in Preparation Example 1 was used.

Comparative Example 3

[0089] The copolycarbonate was prepared by the same method as in Comparative Example 1, except that AP-PDMS (n=34) prepared in Preparation Example 1 was not used.

Experimental Example: Confirmation of Characteristics of Copolycarbonate

[0090] The weight average molecular weight of the copolycarbonates prepared in the examples and comparative examples were measured by GPC using PC Standard with Agilent 1200 series.

[0091] In addition, with respect to 1 part by weight of the respective copolycarbonates prepared in the examples and comparative examples, 0.050 parts by weight of tris(2,4-di-tert-butylphenyl)phosphite, 0.010 parts by weight of octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, and 0.030 parts by weight of pentaerythritol tetrastearate were added

thereto, and the resulting mixture was pelletized using a $\Phi 30$ mm twin-screw extruder provided with a vent, and was injection-molded at a cylinder temperature of 300°C and a mold temperature of 80°C using an injection molding machine N-20C (JSW, Ltd.) to prepare a desired specimen.

[0092] The characteristics of the above specimens were determined in the following manner and the results were shown in Table 1 below.

1) Chemical resistance: the tensile stress (kg/cm^2) was measured (TS_0) in accordance with ASTM D638 (specimen thickness: 3.2 mm). Then, after selecting a solvent as shown in Table 1 below, experiments were conducted based on JIG Strain R1.0 in accordance with ASTM D543 (PRACTICE B). A cotton cloth (2 cm x 2 cm) was placed on the center of each specimen at room temperature (23°C). The solvent was dropped on the cloth enough to be volatilized every day and the specimen was in contact with the solvent for 168 hours. After the experiment was completed, the solvent on the specimen was completely removed with a clean cloth, and the tensile stress was again measured (TS) in accordance with ASTM D638 to calculate TS/TS_0 .

2) Impact strength at room temperature: measured at 23°C in accordance with ASTM D256 (1/8 inch, Notched Izod).

3) Impact strength at low temperature: measured at -30°C in accordance with ASTM D256 (1/8 inch, Notched Izod).

4) Melt index (MI): measured in accordance with ASTM D1238 (conditions of 300°C and 1.2kg).

[Table 1]

		Example 1	Example 2	Comparative Example 1	Comparative Example 2	Comparative Example 3
Chemical resistance (solvent)	Standard	1	1	1	1	1
	HCl	0.99	0.99	0.99	0.98	0.89
	NaOH	0.98	0.97	0.97	0.94	0.90
	Ethyl Acetate	0.93	0.89	0.74	0.76	0.63
(TS/TS ₀)	MeOH	1	1	0.99	0.95	0.91
	Toluene	0.56	0.53	0.41	0.50	0.37
Impact strength at room temperature (J/m)		889	839	651	802	870
Impact strength at low temperature (J/m)		731	718	533	679	194
Weight average molecular weight		30,200	29,800	24,900	28,900	31,300
Melt index (g/10 min)		8	9	12	10	11

[0093] As shown in Table 1 above, the copolycarbonate according to the present invention (Examples 1 and 2) exhibited superior chemical resistance as compared with Comparative Examples 1 to 3, and particularly, the difference was significant when ethyl acetate and toluene were used as the solvent. Also, examples exhibited superior impact strength at low temperature and impact strength at room temperature as compared with comparative examples.

[0094] Accordingly, it could be confirmed that the copolycarbonate according to the present invention exhibited improved chemical resistance and impact strength simultaneously.

Claims

1. A copolycarbonate comprising an aromatic polycarbonate-based first repeating unit; and one or more aromatic polycarbonate-based second repeating units having siloxane bonds, and the copolycarbonate satisfies the following Equation 1:

[Equation 1]

$$TS/TS_0 \geq 0.80$$

in the Equation 1,

TS_0 is tensile stress measured in accordance with ASTM D638, and
 TS represents tensile stress measured in accordance with ASTM D638, after contacted with ethyl acetate for
 168 hours in accordance with ASTM D543 (PRACTICE B).

2. The copolycarbonate of claim 1, wherein the copolycarbonate satisfies the Equation 2 below:

[Equation 2]

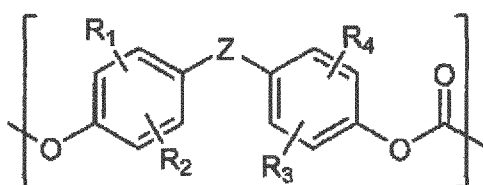
$$TS/TS_0 \geq 0.50$$

in the Equation 2,

TS_0 is tensile stress measured in accordance with ASTM D638, and
 TS represents tensile stress measured in accordance with ASTM D638, after contacted with toluene for 168
 hours in accordance with ASTM D543 (PRACTICE B).

3. The copolycarbonate of claim 1, wherein the copolycarbonate has an impact strength at low temperature of 600 to 1000 J/m as measured at -30°C in accordance with ASTM D256 (1/8 inch, Notched Izod).
4. The copolycarbonate of claim 1, wherein the copolycarbonate has impact strength at room temperature of 840 to 1000 J/m as measured at 23°C in accordance with ASTM D256 (1/8 inch, Notched Izod).
5. The copolycarbonate of claim 1, wherein the copolycarbonate has a weight average molecular weight of 1,000 to 100,000 g/mol.
6. The copolycarbonate of claim 1, wherein the copolycarbonate comprises two kinds of aromatic polycarbonate-based second repeating units having siloxane bonds.
7. The copolycarbonate of claim 1, wherein the first repeating unit is represented by the following Chemical Formula 1:

[Chemical Formula 1]



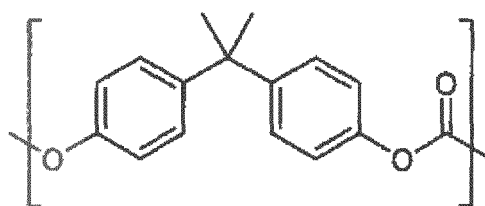
in the Chemical Formula 1,

R_1 , R_2 , R_3 , and R_4 are each independently hydrogen, C_{1-10} alkyl, C_{1-10} alkoxy, or halogen, and
 Z is C_{1-10} alkylene unsubstituted or substituted with phenyl, C_{3-15} cycloalkylene unsubstituted or substituted
 with C_{1-10} alkyl, O, S, SO, SO_2 , or CO.

8. The copolycarbonate of claim 7, wherein the repeating unit represented by Chemical Formula 1 is derived from one or more aromatic diol compounds selected from the group consisting of bis(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl)ether, bis(4-hydroxyphenyl)sulfone, bis(4-hydroxyphenyl)sulfoxide, bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)ketone, 1,1-bis(4-hydroxyphenyl)ethane, bisphenol A, 2,2-bis(4-hydroxyphenyl)butane, 1,1-bis(4-hydroxyphenyl)cyclohexane, 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane, 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane, 2,2-bis(4-hydroxy-3-bromophenyl)propane, 2,2-bis(4-hydroxy-3-chlorophenyl)propane, 2,2-bis(4-hydroxy-3-methylphenyl)propane, 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, bis(4-hydroxyphenyl)diphenylmethane, and α,ω -bis[3-(o-hydroxyphenyl)propyl]polydimethylsiloxane.
9. The copolycarbonate of claim 7, wherein the Chemical Formula 1 is represented by the following Chemical Formula

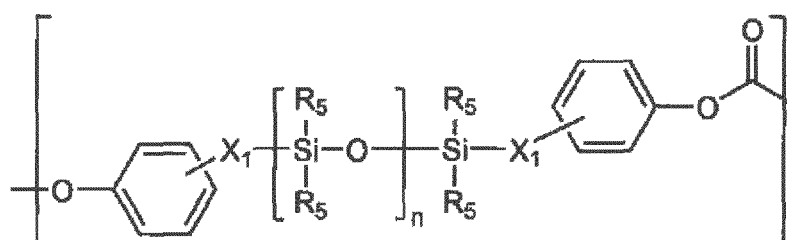
1-1:

[Chemical Formula 1-1]



10. The copolycarbonate of claim 1, wherein the second repeating unit comprises a repeating unit represented by the following Chemical Formula 2 and a repeating unit represented by the following Chemical Formula 3:

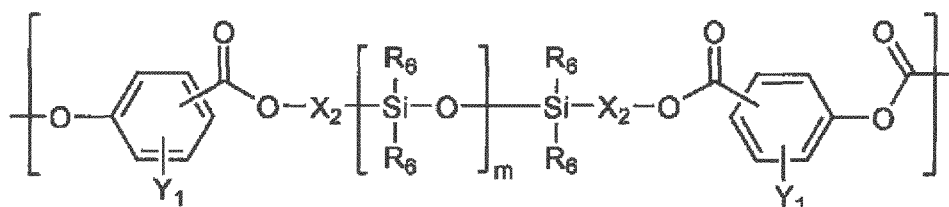
[Chemical Formula 2]



in the Chemical Formula 2,

each of X_1 is independently C_{1-10} alkylene,
 each of R_5 is independently hydrogen; C_{1-15} alkyl unsubstituted or substituted with oxiranyl, oxiranyl-substituted C_{1-10} alkoxy, or C_{6-20} aryl; halogen; C_{1-10} alkoxy; allyl; C_{1-10} haloalkyl; or C_{6-20} aryl, and
 n is an integer of 10 to 200,

[Chemical Formula 3]



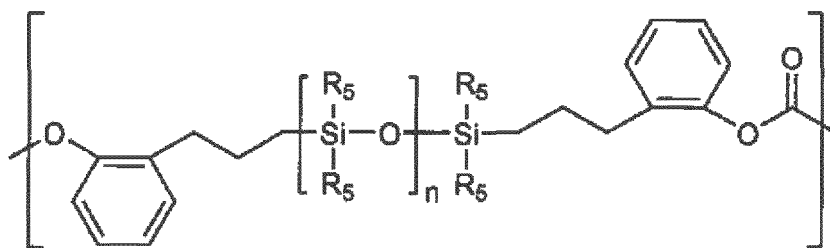
in the Chemical Formula 3,

each of X_2 is independently C_{1-10} alkylene,
 each of Y_1 is independently hydrogen, C_{1-6} alkyl, halogen, hydroxy, C_{1-6} alkoxy, or C_{6-20} aryl,
 each of R_6 is independently hydrogen; or C_{1-15} alkyl unsubstituted or substituted with oxiranyl, oxiranyl-substituted C_{1-10} alkoxy, or C_{6-20} aryl; halogen; C_{1-10} alkoxy; allyl; C_{1-10} haloalkyl; or C_{6-20} aryl, and
 m is an integer of 10 to 200.

11. The copolycarbonate of claim 10, wherein a weight ratio of the repeating unit represented by Chemical Formula 2 and the repeating unit represented by Chemical Formula 3 is 1:99 to 99:9.

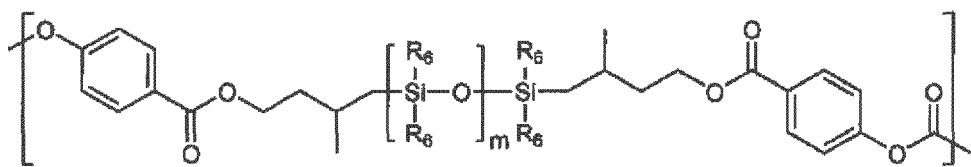
12. The copolycarbonate of claim 10, wherein the repeating unit represented by Chemical Formula 2 is represented by the following Chemical Formula 2-2:

[Chemical Formula 2-2]



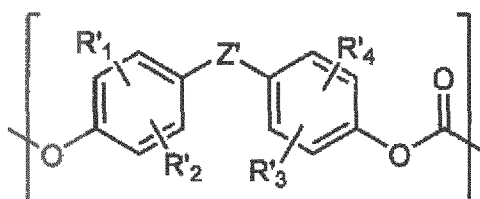
13. The copolycarbonate of claim 10, wherein the repeating unit represented by Chemical Formula 3 is represented by the following Chemical Formula 3-2:

[Chemical Formula 3-2]



14. A polycarbonate composition comprising the copolycarbonate of any one of claims 1 to 13 and a polycarbonate.
15. The polycarbonate composition of claim 14, wherein the polycarbonate comprises a repeating unit represented by the following Chemical Formula 4:

[Chemical Formula 4]



in the Chemical Formula 4,

R'_1 , R'_2 , R'_3 and R'_4 are each independently hydrogen, C_{1-10} alkyl, C_{1-10} alkoxy, or halogen, and Z' is C_{1-10} alkylene unsubstituted or substituted with phenyl, C_{3-15} cycloalkylene unsubstituted or substituted with C_{1-10} alkyl, O, S, SO, SO_2 or CO.

16. The polycarbonate composition of claim 14, wherein a polysiloxane structure is not introduced in a main chain of the polycarbonate.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2015/012291

A. CLASSIFICATION OF SUBJECT MATTER

C08G 64/38(2006.01)i, C08G 64/18(2006.01)i, C08G 77/448(2006.01)i, C08L 69/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G 64/38; C08G 77/448; C08K 7/02; C08K 5/5399; C08L 69/00; C08G 77/38; C08L 83/10; C08K 5/521; C08G 64/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Utility models and applications for Utility models: IPC as above

Japanese Utility models and applications for Utility models: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS (KIPO internal) & Keywords: aromatic polycarbonate, tension stress, ethylene acetate, toluene, low temperature impact strength, room temperature impact strength, weight-average molecular weight, polysiloxane, ASTM D543, ASTM D638

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	KR 10-2014-0116921 A (SABIC GLOBAL TECHNOLOGIES B.V.) 06 October 2014 See paragraphs [0057]-[0064]; claims 1 and 3; and table 5.	1-16
A	WO 2013-175445 A2 (SABIC INNOVATIVE PLASTICS IP B.V.) 28 November 2013 See paragraphs [0011]-[0014], [0037]-[0042], [0067]-[0071] and [0108].	1-16
A	KR 10-2014-0027199 A (SABIC INNOVATIVE PLASTICS IP B.V.) 06 March 2014 See paragraphs [0005]-[0024], [0042]-[0047], [0164]-[0166] and [0231]-[0236].	1-16
A	JP 3457805 B2 (MITSUBISHI ENGINEERING PLASTICS CORPORATION) 20 October 2003 See paragraphs [0006]-[0015] and [0032]-[0035].	1-16
A	KR 10-2007-0098827 A (GENERAL ELECTRIC COMPANY) 05 October 2007 See paragraphs [0045]-[0075] and [0193]-[0204]; and tables 4 and 6.	1-16

☐ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

24 FEBRUARY 2016 (24.02.2016)

Date of mailing of the international search report

25 FEBRUARY 2016 (25.02.2016)

Name and mailing address of the ISA/KR


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Authorized officer

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR2015/012291

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